A predictive model for the enthalpies of hydration of zeolites

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ABSTRACT

A compilation of the average hydration enthalpies per mole of water of 145 diversely originating zeolites measured using different technical methods [76 data from transposed-temperature drop calorimetry (TTDC), 57 data from immersion calorimetry (IC), 6 data from phase equilibria (PE), 5 data from gas-adsorption calorimetry (GAC), and 3 data from hydrofluoric acid solution calorimetry (HF)] was generated. Statistical regressions between three parameters involving the average hydration enthalpy per mole of water \( \Delta H_{\text{hyd-W}}(\text{site A})_{\text{aq}} \), \( \Delta H_{\text{hyd-W}}(\text{site A})_{\text{aq}}(\text{Al}/\text{Si}) \), and hydrated zeolite, \( \text{FD}_{\text{hydr}} \); (4) the average cation electronegativity in the exchange site characterized by parameter \( \Delta E_{\text{hydr}}/(\text{Al}/\text{Si}) \); and (5) the intracrystalline water porosity (WP) determined from the volume of liquid water that can be recovered upon thorough outgassing of the hydrated zeolite. The regressions were performed by taking into account either the nature of the measurement technique, or the nature of the zeolite family. Within the zeolites from the TTDC and IC populations (133 data), the best results were obtained with ln\[−\Delta H_{\text{hyd-W}}(\text{Al}/\text{Si})\] and \( \text{Al}/(\text{Al} + \text{Si}) \). Whatever the measurement technique, considering the nature of the zeolite family having a constant framework density of the anhydrous form and the enthalpy of hydration can be expressed as follows:

\[
\Delta H_{\text{hyd-W}} = -(\text{Al}/\text{Si})^e^{5.491 - 4.674\times(\text{Al}/(\text{Al} + \text{Si}))}
\]

This general relationship can be improved by considering the following parameters: \( \text{FD}_{\text{hydr}} \), \( \Delta H_{\text{hyd-W}}(\text{site A})_{\text{aq}} \), WP and a new parameter that is the product of three parameters \( \text{Al}/\text{Si} \), \( \Delta H_{\text{hyd-W}}(\text{site A})_{\text{aq}} \), and WP weighing the variation of the water porosity related to the nature of the cation and to the total charge of the exchange site. Therefore, an understanding of the chemical formulae and unit-cell volumes of anhydrous and hydrated zeolites is required to evaluate the enthalpy of hydration with an accuracy of ±3.25 kJ/mol H₂O.

Keywords: Hydration enthalpy, integral hydration enthalpy, zeolites, framework density, anhydrous zeolites, hydrated zeolites, thermal stability, water porosity, zeolite X, zeolite Y

INTRODUCTION

Zeolites are microporous minerals with large extra-framework sites that incorporate both exchangeable cations and water molecules. Equilibrium in the zeolite–H₂O system affects the stability and efficiency of zeolites as adsorbing agents, cation exchangers, catalysts, or molecular sieves. The response of zeolites to changes in temperature and/or water vapor pressure is of great interest in a large variety of natural and technological environments. Studies of the hydration-dehydration behavior of zeolites can be used to determine hydration energetics and to predict hydration states as a function of temperature and \( P_{\text{H₂O}} \).

By measuring the enthalpy of dehydration of cordierite, Carey and Navrotsky (1992) showed for the first time a relationship between the enthalpy of hydration and \( \text{Al}/\text{H}_2\text{O} \) (ratio of the frame-